

Selective cleavage of the C–O bonds in alcohols and asymmetric ethers by dissociative electron attachment

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Dissociative electron attachment spectra of 20 saturated compounds containing ether and hydroxyl groups are presented. Two groups of fragmentation processes are identified:

(i) one or two bands mediated by shape resonances in the 1–5 eV range and (ii) three bands (often overlapping) in the 5–12 eV range, assigned to Feshbach resonances with a hole in either the oxygen ‘nonbonding’ orbitals n_O or \bar{n}_O , or in one of the available σ orbitals. The main result of this paper is the discovery of unexpected selectivity in the cleavage of C–O bonds in asymmetric ethers, R_1-O-R_2 , within the range of the σ -Feshbach resonances, where the loss of a neutral alkyl group, R_1 , peaks at a given energy (9.1, 8.4, 8.0 and 8.8 eV for R_1 = ethyl, propyl, butyl and *t*-butyl, respectively), independently of R_2 in all compounds studied. This empirical rule indicates an unexpected conclusion, that the excitation (a hole and two excited electrons) of Feshbach resonances responsible for the fragmentation is spatially localized on one alkyl group or the other. This interpretation is supported by correlation with ionization energies of the alkanes, R_1H . The methyl group behaves differently from the larger alkyl groups—it is not split off at all (except in methanol), thus acting as a ‘protective group’. A number of other observations were made: the previously observed lack of cleavage of C–O bonds (in contrast to O–H bonds) in the n_O and \bar{n}_O Feshbach resonance bands was confirmed in all compounds containing one oxygen atom, but it is now shown that the C–O bond can be broken under certain circumstances in compounds with two oxygen atoms, either in cyclic hydrogen-bonded structures or when the neutral fragment contains oxygen.

I. Introduction

Dissociative electron attachment (DEA),



is a primary process causing chemical changes in collisions of low-energy ($E_i < 15$ eV) electrons with molecules. DEA on isolated molecules is consequently of key importance in the chemistry of natural and technological plasmas.¹ DEA also occurs, in a somewhat modified but closely related form, in the condensed phase, where it plays an important role in radiation-induced damage to living tissue² and in nano-fabrication technologies like focused electron beam induced processing (FEBIP).³

A significant cross section results only when the DEA proceeds resonantly, that is, at suitable electron energies, E_i , where an intermediate short-lived anion $\{AB\}_j^-$ (also called a resonance) is formed in its ground or electronically excited state, j .

The present paper is concerned with the assignment of such resonances and with clarification of their dissociation mechanisms. It focuses on Feshbach resonances,⁴ which involve core excitation and temporary occupation of Rydberg-like^{5,6} orbitals. They lie in the 5–15 eV energy region and, because of their autodetachment lifetime, which is typically longer than that of shape resonances, often make a substantial contribution

to the overall DEA. The understanding of these resonances is more complicated, and generally less advanced, than the understanding of the shape resonances (with the core in its electronic ground state) at lower energies.

To facilitate the assignment and understanding of the DEA bands mediated by Feshbach resonances, we choose to work with saturated compounds, thus avoiding the complications due to the often very pronounced shape resonances that are associated with the temporary occupation of π^* orbitals, and with core excited resonances associated with valence (π , π^*) excited states.

Previously published results related to the present work primarily concern small alcohols, in particular the work on methanol by Kühn *et al.*⁷ and Curtis and Walker,⁸ and the work on methanol and ethanol by Prabhudesai *et al.*,⁹ including a recent measurement of absolute cross sections,^{10,11} and on ethanol by Orzol *et al.*¹² This work revealed, mainly through the study of partially deuterated compounds, various kinds of selectivity. This selectivity can also be found in a slightly weakened form, in the condensed phase.¹³ A more detailed account of the previous work can be found in our earlier publications.^{14–17}

Our own earlier work on a series of larger alcohols and ethers has already yielded a number of conclusions:

– Two groups of fragmentation processes were identified in all compounds: (i) one or two bands in the 1–5 eV range, mediated by shape resonances¹⁵ and (ii) three bands, at around 6.5, 7.5 and 8–11 eV. Following the early assignment in

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methanol^{16,18} and using the energies of the grandparent cation states as a guide,^{14,15} the latter three bands were assigned to Feshbach resonances with a hole in either the oxygen nonbonding orbitals n_O or \bar{n}_O (subsequently called n - and \bar{n} -Feshbach resonances, respectively), or in one of the many σ orbitals (subsequently called σ -Feshbach resonances). The prototypes of the n_O and \bar{n}_O orbitals are the $1b_1$ and $3a_1$ orbitals of H_2O .^{6,19}

- Metastable $(M-1)^-$ ions were identified, which subsequently lost one or two H_2 molecules.^{15,16} Deuteration studies revealed that the hydrogens are lost in a 1,2-fashion, that is, HD is lost from CD_3CH_2OH .²⁰

- A general rule was observed, whereby the C–O bond (in contrast to the O–H bond) is not broken *via* the n - and \bar{n} -Feshbach resonances; it is cleaved only *via* the σ -Feshbach resonances. The rule was rationalized with help of the potential surfaces of the parent Rydberg states.¹⁷

- The shape resonance bands are weak and exhibit a dramatic isotope effect in the small alcohols, but become stronger and may even dominate the spectra for diols.¹⁵

The present work extends the earlier efforts, primarily to higher energies, and is concerned with assignments and phenomena within the manifold of the σ -Feshbach resonances.

II. Experimental and theoretical methods

The dissociative electron attachment spectrometer used to measure the yield of mass-selected stable anions as a function of the electron energy has been described previously.^{15,21,22} It employs a magnetically collimated trochoidal electron monochromator²³ to prepare a beam of quasi-monoenergetic electrons, which is directed into a target chamber filled with a quasi-static sample gas. Fragment anions are extracted at 90° by a three cylinder lens and directed into a quadrupole mass spectrometer. With appropriate setting of the deflection voltages in the ion lens, the spectrometer is capable of detecting even the light H^- ion. The yield of H^- and D^- ions from a number alcohols has already been reported in our previous work,¹⁵ however, and will not be presented here. The yield of H^- from the larger ethers studied in this work was very weak and this paper does not show any H^- spectra. The energy scale was calibrated on the onset of the O^-/CO_2 signal at 4.0 eV. The electron current was around 100 nA and the resolution about 150 meV.

All substances presented in this article are commercially available, except dibutoxy methane which was synthesized in Fribourg. The commercial samples were supplied by Sigma–Aldrich and were used as delivered, without any further purification.

The calculations presented in this article were performed with the quantum chemical package GAUSSIAN 03.²⁴ Threshold energies for various fragmentations were calculated as the differences of the total energies of the products and the targets at 0 K, corrected for the zero point vibrational energy, using the density functional theory (DFT) B3LYP/6-311+G(2df,2p) model, also used for geometry optimizations. The molecular orbitals were calculated at the HF/6-31G(d)

level of theory and the ionization energies with the outer valence Green’s function method.

III. Results and discussion

A Cleavage of the C–O and O–H bonds in alcohols

Fig. 1 shows the yields of the OH^- ion (cleavage of the C–O bond) and the $(M-1)^-$ ion (cleavage of the O–H bond) for ethanol, 1-propanol, *n*-butanol and *t*-butanol. The $(M-1)^-$ yield from ethanol, at the bottom of the figure, is consistent with our previous work¹⁵ and exemplifies the processes mentioned in the introduction—the shape resonance band at 2.8 eV, and the n -, \bar{n} - and σ -Feshbach resonance bands, at 6.3, 7.85 and 9.1 eV, respectively. The \bar{n} -Feshbach resonance appears only as a shoulder on the low-energy side of the 9.1 eV band in Fig. 1, but the yield of D^- from C_2H_5OD ¹⁵ shows this band very clearly as a separate feature, distinct from the 9.1 eV band.

Our results for ethanol are not fully consistent with those of Orzol *et al.*:¹² all DEA bands in their work appear at energies about 1 eV lower than ours (both ref. 15 and this work). Further, we do not observe the broad O^- band which they reported at 5.5 eV. Our energy-scale calibration receives support from the fact that our energies for the H^- and D^- bands from ethanol (in ref. 15, not shown here) are consistent with those of Prabhudesai *et al.*,^{9,10} and from the good agreement of the 2.8 eV onset with the known thermochemical threshold.

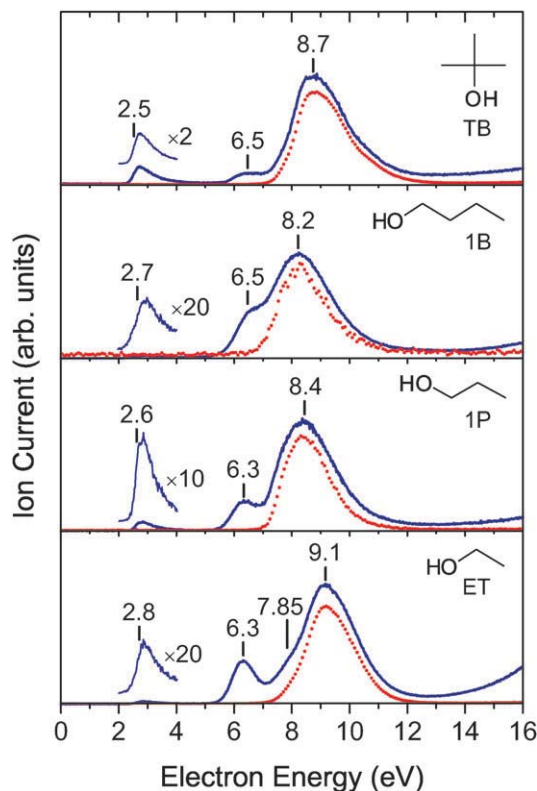


Fig. 1 Comparison between the DEA spectra for OH^- (dotted line) and $(M-1)^-$ anions (solid line) for ethanol (ET), 1-propanol (1P), 1-butanol (1B) and *t*-butyl alcohol (TB).

The absence of the shape resonance and of the n - and \bar{n} -Feshbach resonances in the OH^- yield, shown by the dotted line at the bottom of Fig. 1, shows that cleavage of the C–O bond is not permitted *via* these resonances. This observation was reported and rationalized in our earlier work.¹⁷ The present work is concerned primarily with the band assigned to σ -Feshbach resonances, which is at 9.1 eV in ethanol.

The remaining spectra in Fig. 1 show that the energy of this band is sensitive to the size of the alkyl group—it drops in energy, by nearly 1 eV, when going from ethyl to butyl. The energy of the lower-lying bands remain essentially unchanged; only their relative intensities change. The shape resonance band does not shift substantially because its energy is determined by the thermochemical threshold, given by the O–H bond dissociation energy and the electron affinity of the alkoxy radical, none of which changes appreciably when going from ethyl to butyl. The n -Feshbach resonance band remains essentially unchanged at 6.3 eV, its localization on the oxygen atom makes it insensitive to the size of the alkyl substituent. The \bar{n} -Feshbach resonance is obscured by the σ -Feshbach resonances in the upper three spectra.

B Loss of neutral alkyl radicals in ethers and alcohols

The cleavage of the C–O bond in ethers follows the same rules as the cleavage of the C–O bond in alcohols in the Feshbach resonance region, in the sense that the n - and \bar{n} -Feshbach resonances do not cleave this bond, and only the band due to σ -Feshbach resonances appears in the spectra.^{16,17} This section studies trends and regularities in the latter band in a long series of compounds, both alcohols and ethers. The result is an unexpected observation—that the energy of the σ -Feshbach resonance band depends *only* on the neutral fragment which is formed in the DEA, and *does not depend on the remainder of the target molecule*. This is best illustrated when spectra are not grouped in the usual way, sorted by a given target molecule, but when spectra from a range of targets resulting in the same neutral fragment are presented in one picture.

The first example is the formation of the ethyl radical from ethanol and six different ethers, shown in Fig. 2 and 3, where the band due to the σ -Feshbach resonance is at the same energy of about 9.1 eV, despite the varying structures of the precursors. Two more examples of ethyl radical loss from more complex targets will be presented in section III E (Fig. 10) and the bands also appear at the same energy.

Fig. 4 shows DEA spectra where the neutral fragment is the n -propyl radical, with propanol and two different ethers as precursors. Again, the bands are at the same energy for all precursors, but this energy is about 0.7 eV lower than when ethyl is the neutral fragment! Since the propyl chain is the only chemical similarity between these three molecules, we conclude that the excitation in the Feshbach resonances associated with the 8.5 eV band is localized on the propyl moiety (but delocalized over the length of the propyl chain), and does not sample the other alkyl substituent.

The results for the loss of the n -butyl radical are shown in Fig. 5 and the bottom two spectra of Fig. 6. Again, the energies of the bands are about the same and are about

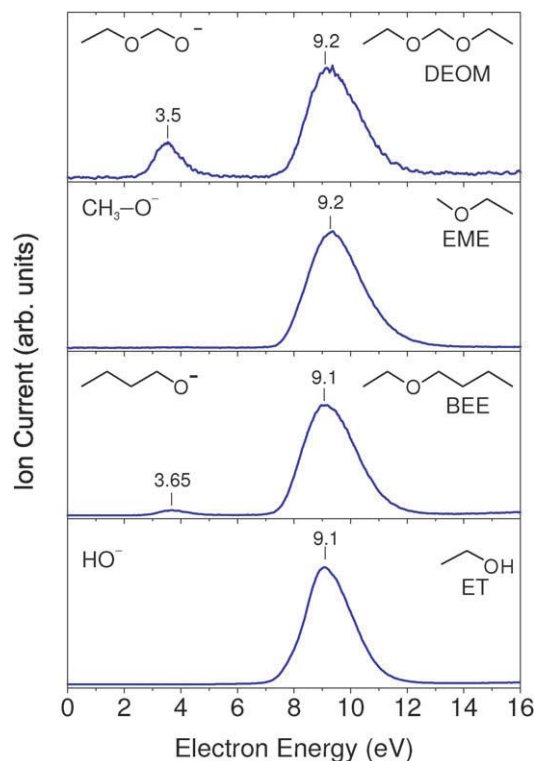


Fig. 2 DEA spectra for the loss of neutral ethyl radical from ET, butyl ethyl ether (BEE), ethyl methyl ether (EME) and diethoxy methane (DEOM). The initial molecule is shown in the right corner, and the resulting anion in the left corner of each spectrum.

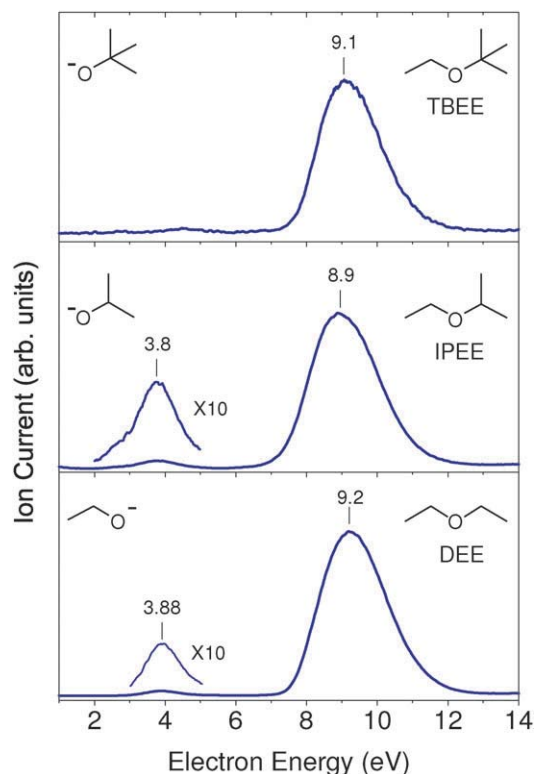


Fig. 3 DEA spectra for the loss of neutral ethyl radical from diethyl ether (DEE), isopropyl ethyl ether (IPEE) and *t*-butyl ethyl ether.

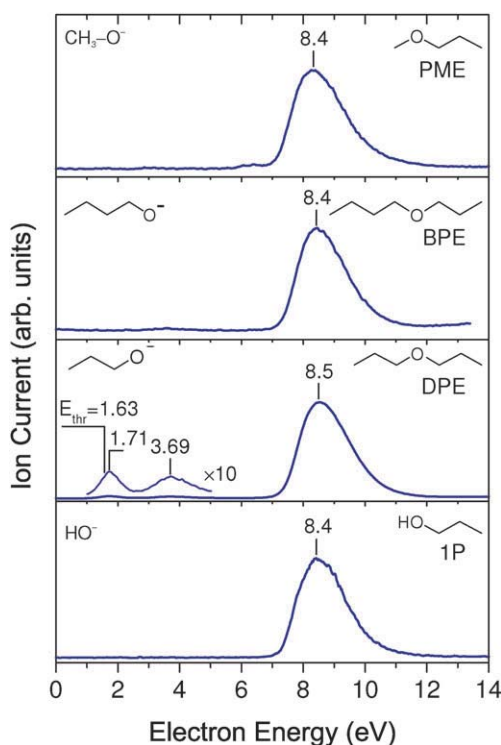


Fig. 4 DEA spectra for loss of propyl neutral fragment from 1P, dipropyl ether (DPE), butyl propyl ether (BPE) and propyl methyl ether (PME). The calculated threshold energy, E_{thr} , is indicated for DPE.

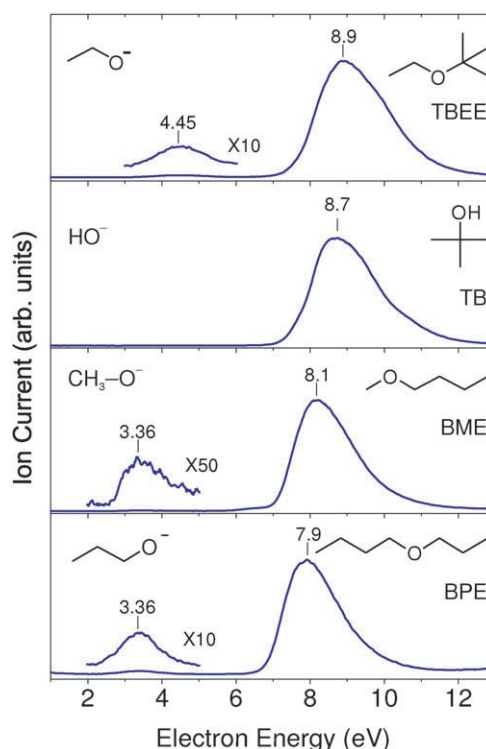


Fig. 6 DEA spectra for loss of *n*-butyl (bottom two panes) and *t*-butyl (top two panes) neutral fragments from BPE, butyl methyl ether (BME), TB and *t*-butyl ethyl ether (TBEE).

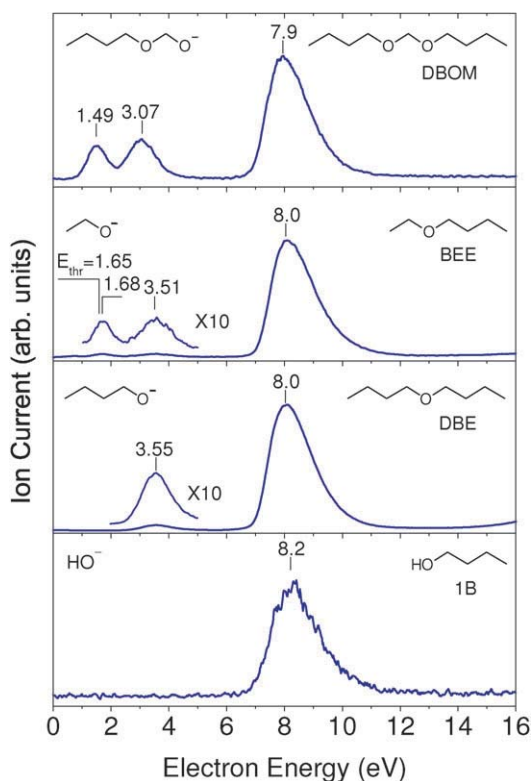


Fig. 5 DEA spectra for loss of *n*-butyl neutral fragment from 1B, dibutyl ether (DBE), BEE and dibutoxy methane (DBOM). The calculated threshold energy, E_{thr} , is indicated for BEE.

0.4 eV lower than those for loss of the *n*-propyl radical. Two more examples of *n*-butyl radical loss will be presented in section III E (Fig. 10) and the bands also appear at the same energy.

Finally, the top two spectra in Fig. 6 show loss of the *t*-butyl radical. The band is at an energy about 0.7 eV higher than that for the loss of the *n*-butyl radical.

Note that some targets are shown twice in the above figures, for example butyl ethyl ether (BEE) in Fig. 2 (loss of ethyl) and Fig. 5 (loss of butyl). A band due to σ -Feshbach resonances appears in both spectra, but its energy is different: 8 eV for loss of butyl and 9.1 eV for loss of ethyl. This suggests that two different resonances are responsible for the bands in the two spectra and that these resonances are localized on different alkyl moieties of the molecule. This energy difference of about 1 eV also raises the possibility of controlling the dissociation of this molecule by changing the energy of the electron, although the practical usefulness is strongly limited by the fact that the shifts are less than the widths of the anion peaks.

The extensive data mentioned above indicates an empirical rule whereby the σ -Feshbach resonance band appears at nearly the same energy for the loss of a given neutral fragment, independent of the structure of the remainder of the precursor. This rule is very unexpected. It cannot be due to different threshold energies—all processes are well above threshold.

C Comparison with photoelectron spectra

In our earlier work we assigned DEA bands to specific Feshbach resonances guided by comparison with the grandparent states in the photoelectron spectrum of the target

molecules.^{14,15,17} This approach was useful in assigning the n - and \bar{n} -Feshbach resonances, and the σ -Feshbach resonances in small molecules like methanol. It is not useful in the present case of σ -Feshbach resonances in large molecules, however. The photoelectron spectra reveal many closely spaced, strongly overlapping bands (in jargon sometimes called ‘the σ -mountain’), associated with ionization from σ_{C-C} and σ_{C-H} orbitals—there are no distinct isolated photoelectron bands which could be uniquely associated with a given DEA band. The many overlapping σ bands in the photoelectron spectrum are in contrast to the striking simplicity of the DEA bands, which have only one band for each alkyl fragment.

Even more importantly, the energies and number of the σ photoelectron bands are different for different target molecules; they depend on the structure of the entire molecule. Thus, they fail to reproduce the striking observation of the present work that the energies of the DEA bands are the same for a whole range of target molecules provided that the same alkyl fragment is lost.

There is therefore no useful correlation between the present DEA bands and the photoelectron spectra of the entire target molecules, the ethers and the alcohols. On the other hand, we wish to point out that there is, an initially unexpected, correlation with the photoelectron spectra of the alkanes corresponding to the alkyl substituents in the present ethers and alcohols.

The photoelectron spectra are given in ref. 19. Table 1 shows that the 1st vertical ionization energies of the alkanes correlate very well with the energies of the DEA bands corresponding to the loss of the corresponding alkyl substituents—the energy difference is a nearly constant 3 eV—across a whole range of target molecules. (The only deviation is the value $\Delta E = 2.4$ eV for the *t*-butyl. This could

Table 1 Summary of results for the band due to σ -Feshbach resonances in molecules of the type R_1OR_2 . For each R_1 , the position of the σ -Feshbach resonance (E_{FR}) is given, as observed in the yield of the fragment R_2O^+ , that is, the loss of neutral R_1 . These values are, for a given R_1 , nearly independent of R_2 and their mean, over all available substituents R_2 , is given. The first vertical ionization energies, IE, of the hydrocarbons, R_1H ,¹⁹ are given in the next column, and the last column lists the differences $\Delta E = IE - E_{FR}$. All values are in eV

R_1	E_{FR}	IE	ΔE
Methyl	10.5	13.6	3.1
Ethyl	9.1	12.0	2.9
Propyl	8.5	11.5	3.0
Butyl	8.0	11.0	3.0
<i>t</i> -Butyl	8.7	11.1	2.4

be related to the reduction of the term values of Rydberg states of alcohols when changing from linear to branched alkyl groups, reported by Robin²⁵ (pages 258–259).)

We take the absence of a useful correlation with the photoelectron spectra of the entire ethers, and the clear correlation with the photoelectron spectra of the alkanes corresponding to the individual alkyl groups, as a further indication that the excitation in the Feshbach resonances responsible for the DEA bands is localized only on one alkyl group or the other, and not distributed over the entire molecule. In other words, in the example of butyl ethyl ether, the Feshbach resonances responsible for the DEA bands do not have a positive ion core equivalent to that observed in photoelectron spectroscopy (*i.e.*, with positive charge distributed over the entire molecule). Instead, we find an indication that the Feshbach resonance responsible for the 8.0 eV band in Fig. 5 consists of a positive ion core with charge distributed only over the butyl moiety, and the Feshbach resonance responsible for the 9.1 eV band in Fig. 2 consists of a positive ion core with charge distributed only over the ethyl moiety. The fragment lost is the one on which the excitation (*i.e.*, the hole and the two associated diffuse electrons) was localized. The negative charge finally resides on the oxygen-containing fragment (which has the higher electron affinity), not on the alkyl fragment on which the original excitation resided.

D Molecular orbitals

Calculations of ionization energies and the shapes of self-consistent field (SCF) orbitals give useful insight into the present subject because of their potential relation to the positive ion core of the Feshbach resonances. Selected results for butyl ethyl ether are shown in Fig. 7.

Assuming that ionizations occur from individual orbitals implies that the shapes of these orbitals give an indication of the shape and spatial extent of the resulting hole in the isolated positive ion. The indication is crude, because of electron redistribution which accompanies ionization, but useful.

The $7a''$ HOMO, the n_O lone pair MO, is calculated to be largely localized on the oxygen atom. The following four ionization energies are closely spaced (and more orbitals, also closely spaced, continue to higher energies, not shown in the figure), emphasizing the high density of states in this energy range—the ‘ σ -mountain’. The $6a''$ MO is localized on the butyl moiety (and delocalized over its entire length), and, thus, has the correct properties to rationalize the 8.0 eV butyl loss

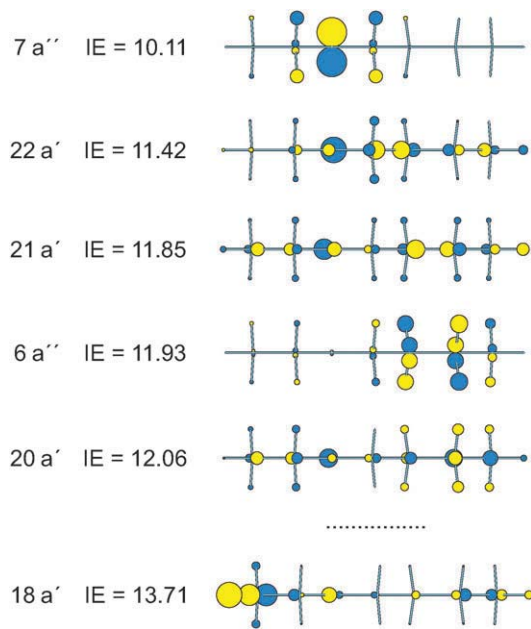


Fig. 7 Diagrams of the top 5 (plus the lower-lying $18a'$) occupied molecular orbitals in butyl ethyl ether within C_s symmetry, drawn with the MOPLOT program.²⁶ The ionization energies are calculated with the outer valence Green’s function method.

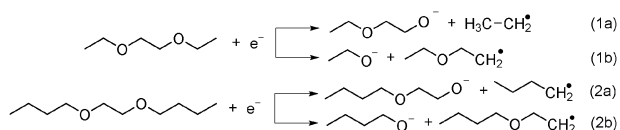


Fig. 8 Reaction scheme for the dissociation of ethylene glycol diethyl ether (EGDE) (1a and 1b) and ethylene glycol di-*n*-butyl ether (EGDB) (2a and 2b).

band in the butyl ethyl ether (BEE) spectrum of Fig. 5, in the sense that it does not ‘probe’ the ethyl substituent. A second such MO, 18a', localized on the ethyl moiety, is also shown in Fig. 7, with a calculated ionization energy of 13.7 eV. On the other hand, the usefulness of these findings is limited by the fact that the majority of the calculated MOs, for example 20a' and 21a' in Fig. 7, are delocalized over the entire molecule and thus not suited to explaining the observation that the energy of the DEA bands depends only on one alkyl substituent and not the other. Also, the difference between the two ionization energies for ionization from the two localized orbitals, 6a'' and 18a', (1.8 eV) is larger than the difference of the two DEA bands (1.1 eV).

Another line of thought which could be attempted here is correlating the DEA bands with the bonding properties of the orbitals. Thus, the 20a' and 21a' orbitals are bonding with respect to the O–butyl bond, and removing an electron from these orbitals could be expected to weaken that bond and lead to loss of a butyl radical. Our earlier work on methanol has demonstrated the limits of this line of thought, however.¹⁷ It has shown that a Feshbach resonance consisting of a hole in a nonbonding *n* orbital, and two electrons, also in a nonbonding 3s orbital, results in a strongly repulsive potential surface, as a result of an avoided crossing with a higher resonance and of Rydberg–valence mixing. Also in the present case, a consideration of the bonding properties of the orbitals does not seem to lead to an explanation of the observed behavior. The 20a' and 21a' orbitals are delocalized over the whole molecule, and not suitable to explain why the band corresponding to loss of the butyl radical is at the same energy for many different molecules.

There is therefore no useful correlation between the σ orbitals and the observed DEA bands in the σ -Feshbach resonance region, in contrast to what was found for the n_O and \bar{n}_O orbitals.

E Compounds with two oxygen atoms

Studying the breaking of the C–O bond in ethers is completed by extending it to more complex compounds, whose structures, experimentally observed reactions and resulting fragments are listed in Fig. 8 and 9. These compounds are discussed separately because they reveal certain extensions of the rules and regularities described in the above sections, which are best discussed when the basis of the above rules is already given.

Fig. 10 shows the DEA spectra for reactions (1a), (2a), (3a) and (4a). The top two spectra correspond to loss of a neutral ethyl radical and belong, in this sense, to the same category as the spectra in Fig. 2 and 3. Similar to those figures, the band

for this reaction appears at 9.0 eV, providing further support for the conclusions made in section III B. The same applies to the loss of a neutral butyl radical in the bottom part of Fig. 10, with a band at 8.0 eV, to be compared with bands at the same energies in Fig. 5 and 6.

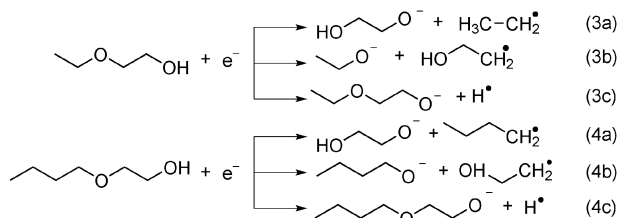


Fig. 9 Reaction scheme for the dissociation of 2-ethoxy ethanol (2EE) (3a, b and c) and 2-butoxy ethanol (2BE) (4a, b and c).

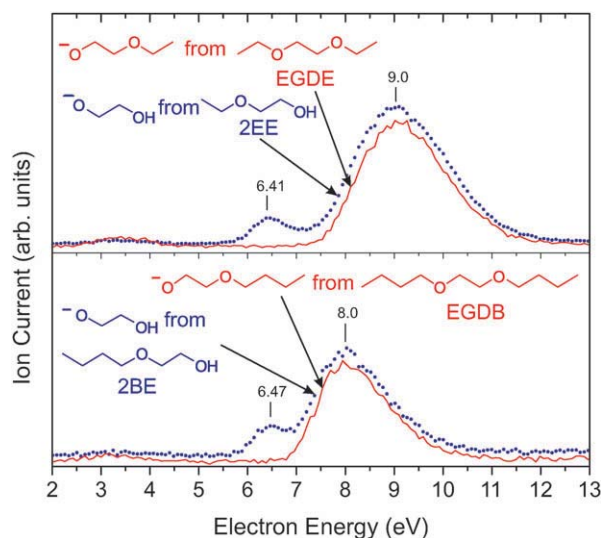


Fig. 10 DEA spectra of EGDE (top, solid line), 2EE (top, dots), EGDB (bottom, solid line) and 2BE (bottom, dots).

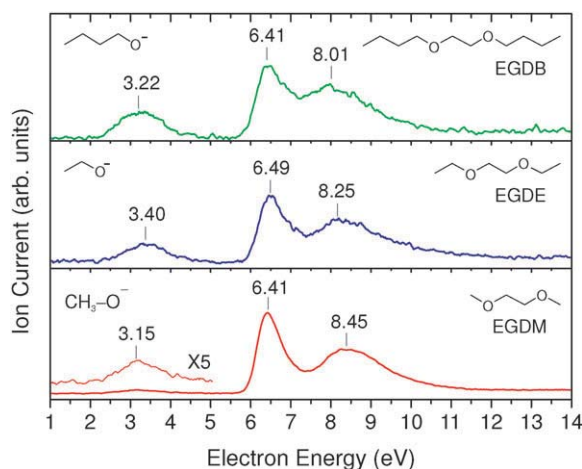


Fig. 11 DEA spectra of EGDB, EGDE and of ethylene glycol dimethyl ether (EGDM). The anions are indicated on the left side of the panel.

The bands at 6.41 and 6.47 eV in Fig. 10 are surprising, because they indicate that the n-Feshbach resonance causes a cleavage of the C–O bond, in contrast to what has been observed with alcohols and simple ethers (Fig. 1 and ref. 17). The fact that this process occurs only in the compounds with a hydroxyl group, 2EE and 2BE in Fig. 10, indicates that it is the hydroxyl group which mediates the cleavage of the ether bond. A decisive point is presumably the intramolecular hydrogen bridge which holds the hydroxyl and the ether oxygens in close proximity in the lowest energy conformation. Our DFT calculations predict, for both molecules, that the hydrogen-bridged cyclic conformations are 10 kJ mol^{−1} more stable than their open chain counterparts. The hydrogen bridge will be even stronger in the anions formed through reactions (3a) and (4a), providing further exothermicity. The presence of a hydrogen bridge appears to reduce or to remove the activation barrier which prevents the cleavage of the C–O bond *via* the 6.5 eV resonance in simple alcohols and ethers.

Fig. 11 shows the DEA spectra for reactions (1b), (2b) and an analogous reaction of ethylene glycol dimethyl ether EGDM. The particularity of these reactions, which were not possible with monoethers, is a cleavage of the C–O bond to form a neutral fragment which is not a simple alkyl radical as discussed in section III B, but which contains an oxygen atom. An example is the 2-butoxy ethyl radical in reaction (2b). Its formation is depicted in the DEA spectrum in the top panel of Fig. 11. DEA spectra involving the formation of other oxygen-containing neutral fragments from ethylene glycol dimethyl and diethyl ethers are shown in the lower panels of Fig. 11. All three spectra in this figure are very similar, and unexpected in the sense that the 6.4 eV n-Feshbach resonance is responsible for cleavage of a C–O bond, in contrast to the observations made with simple alcohols and ethers (ref. 17 and the present work). In this case, it appears that the presence of an oxygen atom in the neutral fragment is responsible for the reduction or the removal of the activation barrier which prevents the cleavage of the C–O bond *via* the 6.4 eV resonance in simple alcohols and ethers.¹⁷

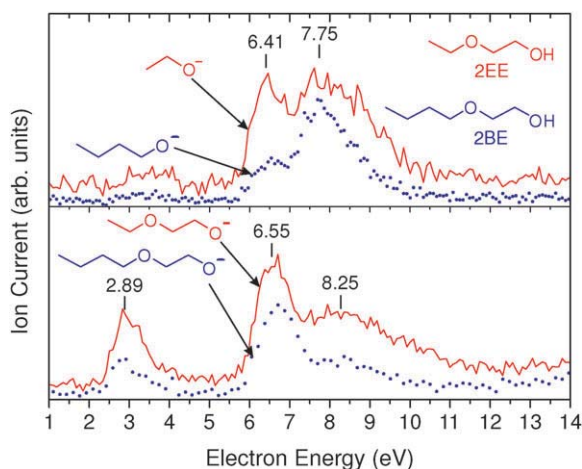


Fig. 12 DEA spectra of 2EE and 2BE. The top panel refers to the reactions (3b) and (4b), while the bottom panel refers to the reactions (3c) and (4c).

The energy of the 8.0–8.5 eV band in Fig. 11 decreases slightly with increasing size of the neutral fragment, an observation already made for the pure alkyl neutral fragments in section III B. The relatively small shift of about 0.2 eV in each step indicates that the effect approaches its asymptotic value—the neutral fragment chains are 4, 5 and 7 atoms long here, longer than the ethyl, propyl and butyl fragments discussed in section III B. The fact that the band shifts at all suggests that the Feshbach resonance is delocalized over the entire butoxy ethyl radical.

For EGDM, the formation of CH₃O[−] (bottom of Fig. 11) is the only observed fragmentation pathway. In particular, a reaction where a neutral methyl fragment is lost was not observed. This further supports the conclusion reached above for simple methyl ethers, *i.e.*, that methyl radical is not lost as a neutral fragment.

The bottom part of Fig. 12 shows the yields of the (M−1)[−] ions from ethoxy- and butoxy ethanol. They are best discussed in comparison with the (M−1)[−] ion yield from unsubstituted ethanol (the solid line in the bottom panel of Fig. 1). The bands near 2.8 and 6.5 eV are nearly identical in all three cases, compatible with their interpretation: the onset of the former band corresponds to the threshold energy, which does not change appreciably. The Feshbach resonance near 6.5 eV is localized on the oxygen and is not affected by changes in substitution far removed from it. On the other hand, the 9.1 eV band of ethanol shifts down to 8.25 eV upon substitution, which is also in line with the interpretation that the excitation in the Feshbach resonance is delocalized over the ethoxy and butoxy moieties.

The top part of Fig. 12 shows breaking of the C–O bond such that the same •CH₂CH₂OH neutral fragment is released for both targets. If the rules reported above for the release of neutral alkyl fragments were valid even for the release of this fragment, then the 7.75 eV band should be at the same energy for both targets, which, within experimental error, is the case.

F Shape resonances

This paper is primarily concerned with Feshbach resonances, but a brief discussion of the shape resonance bands observed in many of the spectra appears appropriate. In alcohols, the shape resonance bands are narrow, with a nearly vertical onset at the threshold energy. They may thus be understood as the dissociation of a σ* resonance which proceeds without an activation barrier, in agreement with our earlier discussion.¹⁵

A brief discussion of the shape resonance bands in diethyl and dibutyl ether was given in our earlier publication.¹⁶ The main conclusions—that the bands do not have a vertical onset, and peak well above the threshold for dissociation (indicating an activation barrier)—are confirmed in the present work. The details of these bands are difficult to rationalize, however. One band around 3.5 eV is often observed, but two bands appear in some cases (Fig. 4 and 5). The lower of these two bands are at a surprisingly low energy for saturated compounds. The onsets of the dissociations appear to occur at thresholds—the calculated threshold values are given in Fig. 4 and 5. This fact may help to explain the unexpected cleavage of ethers by dissociative attachment of a photoexcited trapped electron in

a cryogenic γ -irradiated 3-methylpentane glass.²⁷ The ether used there was dimethyl ether, which does not show low energy bands in the gas phase, but it is possible that solvation stabilizes the resonance, decreasing its autodetachment width and permitting dissociation, even in dimethyl ether.

G Comparison with unsaturated ethers

The present data can be compared to the results on unsaturated ethers of Bulliard *et al.*²⁸ The major difference in respect to the present compounds is the presence of a very pronounced π^* shape resonance at 1–2 eV. The unsaturated compounds fell into two categories, giving very different results:

(a) compounds where the ether oxygen and the π system are separated by a methylene group, that is methyl allyl ether, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\text{CH}_3$, and the benzyl methyl ether, $\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-\text{CH}_3$. In these cases, where the C–O bond to be broken does not lie in the plane of the π system and the π system can conjugate with the σ^* orbital of the C–O bond to be broken, the dissociation of the π shape resonance is symmetry-allowed, occurs rapidly and completely dominates the DEA spectra. Feshbach resonances are not visible in the DEA spectra of these compounds, and there is no evident relation to the processes presented in this work.

(b) Compounds where the ether oxygen and the π system are directly linked (methyl vinyl ether, $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_3$, ethyl vinyl ether $\text{CH}_2=\text{CH}-\text{O}-\text{C}_2\text{H}_5$ and anisole $\text{C}_6\text{H}_5-\text{O}-\text{CH}_3$). In these cases, the C–O bond to be broken lies in the plane of the π system, the π system cannot conjugate with the σ^* orbital of the C–O bond to be broken and the dissociation of the π^* shape resonance is symmetry-forbidden. DEA spectra of these compounds have only relatively weak shape resonance bands in the 2–4 eV range, and prominent Feshbach resonance bands similar to those in the present work.

A ($n, 3s^2$) resonance is observed around 6.5 eV, but, unlike in saturated ethers, this resonance appears to cleave the C–O bond when the C atom is an sp^2 -hybridized carbon of the allyl group. This resonance does not, however, cleave the C–O bond when the C atom is sp^3 -hybridized in the ethyl group, confirming the conclusions reached in ref. 17 and in this work.

A loss of an ethyl radical from ethyl vinyl ether has a broad band around 9.1 eV, the same energy as the loss of an ethyl radical in numerous saturated alcohols and ethers presented in this work.

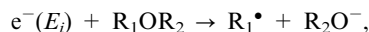
Finally, the loss of the neutral methyl radical has not been observed in methyl vinyl ether, reinforcing the conclusion that the methyl group can be used as a “protective group” to steer the fragmentation in a controlled manner.

IV. Conclusions

Dissociative electron attachment processes in saturated oxygen-containing compounds are mediated by shape resonances, which lead to generally weak fragmentations below 5 eV, and by Feshbach resonances in the 5–11 eV range. The Feshbach resonances have electronic configurations of the type $^2(\psi_i^{-1}, 3s^2)$, and give rise to DEA bands around 6.5 eV (where ψ_i is n_O), 7.5 eV (where ψ_i is \bar{n}_O), and 8–11 eV (where ψ_i is one

of the many available σ orbitals). The \bar{n} -Feshbach band often overlaps with the σ -Feshbach band and cannot always be discerned as a separate band.

The primary result of the present work is the observation of a marked selectivity within the dense manifold of the σ -Feshbach resonances. In the reaction



with R_1 and R_2 being an alkyl radical or an H atom, the energy of the σ -Feshbach band is the same for a given R_1 in many compounds *i.e.* it is independent of the nature of R_2 . The band was observed at 9.1, 8.5 and 8.0 eV for R_1 being ethyl, propyl and butyl radicals, and at 8.7 eV for the *t*-butyl radical, for a wide variety of target molecules.

This has the interesting consequence that one or the other C–O bond can be cleaved preferentially in asymmetric ethers by choosing the appropriate electron energy, and that a given alkyl radical is lost preferentially when electrons of a given energy impact on a wide range of compounds.

These observations are surprising because one would expect that the energy of a Feshbach resonance depends on the nature of the entire target molecule, not only on which neutral radical is formed in the fragmentation. One would also not expect such pronounced selectivity within a dense manifold of very highly excited states of the intermediate negative ion, as the individual states are without doubt strongly vibronically coupled, allowing the system to jump between the different states through numerous conical intersections and by breakdown of the Born–Oppenheimer approximation.

To explain the observations, we have to assume that the excitation (*i.e.*, the hole in the core and the two diffuse electrons) in the Feshbach resonances responsible for DEA is not delocalized over the entire molecule, but only around one alkyl substituent or the other. The conclusion of localized excitation is further supported by the observed correlation between the DEA band energies and the experimental ionization energies of the hydrocarbons R_1H (*i.e.*, not ionization energies of the entire target molecules R_1-O-R_2), which are taken as a measure of the energy required to create a hole on the R_1 part of the molecule.

The observations thus provide evidence for a tendency of σ -Feshbach resonances responsible for DEA in large molecules to localize on only a part of the molecule. This finding could have important implications for localization of damage caused by 8–12 eV electrons in large molecules like DNA or proteins.

The interpretation proposed here is that the 7–12 eV region contains many closely spaced Feshbach resonances, which overlap because of their Franck–Condon widths, with holes in the many σ orbitals available in large molecules. Certain of these Feshbach resonances are localized on a given alkyl moiety, one resonance at R_1 and another at R_2 , and, at the same time, delocalized over the entire length of that moiety. The energy of such a resonance thus depends only on R_1 or R_2 , but not on the remainder of the target molecule. Localized means that the hole in the core, and hence also the two diffuse electrons bound by the positive charge of the hole, are spatially localized on a given part of the target molecule. Next, one

needs to assume that these localized Feshbach resonances cause the fragmentation, and that they dissociate in such a way that the negative charge finally resides on the fragment with the higher electron affinity, which is the one containing the oxygen atom, and not on the alkyl fragment on which the Feshbach resonance was initially localized.

The interpretation is not based on quantum chemical calculations. In fact, theoretical methods applicable to our observations are not available. The problems are the large size of the molecules, the need to calculate highly-excited Feshbach resonances and to understand the nuclear dynamics on a dense manifold of closely spaced electronic states of the transient anion.

We inspected the shapes and the bonding properties of the occupied σ SCF orbitals of butyl ethyl ether, as a potential indicator of the shapes of the holes in the Feshbach resonances, but arrived at the conclusion that they do not provide a useful rationalization of the observations, primarily because they are, in their majority, delocalized over the entire molecule.

We extended the study to compounds of the type $R_1OCH_2CH_2OR_2$ which offer more fragmentation channels, in particular ones where the neutral fragment is not a simple alkyl radical, but also contains an oxygen atom. The above conclusions could be extended even to these cases.

This class of compounds also led to conclusions which are slightly outside of the main focus of this paper, but also interesting. They represent an extension of the rule which states that the ~ 6.5 eV resonance with a hole in the n_O nonbonding MO mediates cleavage of the O–H but not the C–O bond in alcohols and ethers containing only one oxygen atom.¹⁷ The present study reveals that, under certain circumstances, this rule is relaxed in the compounds of the type $R_1OCH_2CH_2OR_2$ with two oxygens, where the ~ 6.5 eV resonance was also found to break, weakly, the C–O bond. This occurred in two cases: (i) when the neutral fragment contained an oxygen atom or (ii) in molecules with $R_2 = H$, when the neutral fragment was a simple alkyl radical but when the most stable conformation of the target molecule had a hydrogen-bonded cyclic structure bringing the hydroxyl and the ether oxygens into close proximity.

The methyl radical behaves differently from other alkyl moieties in all the molecules studied except methanol. Dissociations involving a methyl radical as a neutral product are too weak to be detected, except in the case of methanol, where the OH^- ion is observed. This means that methyl can be used as a “protective group”, to inhibit certain fragmentations.

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References

- 1 L. G. Christophorou and J. K. Olthoff, *Fundamental Electron Interactions with Plasma Processing Gases*, Kluwer Academic, New York, Boston, Dordrecht, London, Moscow, 2004.
- 2 B. Boudaiffa, P. Cloutier, D. Hunting, M. A. Huels and L. Sanche, *Science*, 2000, **287**, 1658.
- 3 I. Utke, V. Friedli, M. Purucker and J. Michler, *J. Vac. Sci. Technol., B*, 2007, **25**, 2219.
- 4 G. J. Schulz, *Rev. Mod. Phys.*, 1973, **45**, 423.
- 5 F. H. Read, *J. Phys. B*, 1977, **10**, 449.
- 6 M. B. Robin, *Higher Excited States of Polyatomic Molecules*, vol. 3, Academic Press, Orlando, 1985.
- 7 A. Kühn, H. P. Fenzlaff and E. Illenberger, *J. Chem. Phys.*, 1988, **88**, 7453.
- 8 M. G. Curtis and I. C. Walker, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2805.
- 9 V. S. Prabhudesai, A. H. Kelkar, D. Nandi and E. Krishnakumar, *Phys. Rev. Lett.*, 2005, **95**, 143202.
- 10 V. S. Prabhudesai, D. Nandi, A. H. Kelkar and E. Krishnakumar, *J. Chem. Phys.*, 2008, **128**, 154309.
- 11 V. S. Prabhudesai, N. B. Ram, G. Aravind, P. Rawat and E. Krishnakumar, *Journal of Physics: Conference Series*, 2007, **80**, 012016.
- 12 M. Orzol, I. Martin, J. Kocisek, I. Dabkowska, J. Langer and E. Illenberger, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3424.
- 13 L. Parenteau, J. P. Jaygerin and L. Sanche, *J. Phys. Chem.*, 1994, **98**, 10277.
- 14 T. Skalický and M. Allan, *J. Phys. B*, 2004, **37**, 4849.
- 15 B. C. Ibănescu, O. May, A. Monney and M. Allan, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3163.
- 16 B. C. Ibănescu, O. May and M. Allan, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1507.
- 17 B. C. Ibănescu and M. Allan, *Phys. Chem. Chem. Phys.*, 2008, **10**, 5232.
- 18 M. Jungen, J. Vogt and V. Staemmler, *J. Phys. B*, 1979, **37**, 49.
- 19 K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Societies Press, Tokyo, 1981.
- 20 B. C. Ibănescu, *Electron-driven chemistry of saturated compounds containing oxygen and nitrogen atoms*, PhD thesis, University of Fribourg, 2009.
- 21 M. Stepanović, Y. Pariat and M. Allan, *J. Chem. Phys.*, 1999, **110**, 11376.
- 22 R. Dressler and M. Allan, *Chem. Phys.*, 1985, **92**, 449.
- 23 A. Stamatovic and G. J. Schulz, *Rev. Sci. Instrum.*, 1968, **39**, 1752.
- 24 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.01)*.
- 25 M. B. Robin, *Higher Excited States of Polyatomic Molecules*, vol. 1, Academic Press, New York, 1974.
- 26 R. V. Otkhov and T. Bally, Moplot version 1.83 <http://www-chem.unifr.ch/tb/moplot/moplot.html>.
- 27 H. Yoshida, M. Irie, O. Shimada and K. Hayashi, *J. Phys. B*, 1972, **76**, 3747.
- 28 C. Bulliard, M. Allan and S. Grimme, *Int. J. Mass Spectrom.*, 2001, **205**, 43.